and *tert*-butyl isocyanide (0.25 mL, 0.0022 mol) was added. The orange suspension was stirred for 4 h, and the precipitate was collected by filtration. The residue was dissolved in toluene (10 mL) and filtered, and the filtrate was concentrated to ca. 5 mL. Cooling (−10 °C) yielded orange-red needles (0.10 g, 91%).

Acknowledgment. We thank the Regents of the University of California for a fellowship (G.S.G.) and the National Science Foundation for a departmental grant used to purchase the NMR spectrometer used in this work.

Note Added in Proof. Some phosphine complexes of the Mo(II) dications have been described recently.[38]

Registry No. $Mo(t\text{-}BuNC)_5(O_2CMe)_2$, 77136-36-8; $[Mo(t\text{-}BuNC)_6(O_2CCF_3)][O_2CCF_3]$, 77136-38-0; $[Mo(t\text{-}BuNC)_6Cl][Cl]$, 66652-50-4; $[Mo(t\text{-}BuNC)_7][PF_6]_2$, 41982-05-2; $[Mo(t\text{-}BuNC)_7][Mo_6O_{19}]$, 77209-24-6; $[Mo(t\text{-}BuNC)_3(O_2CCF_3)_2]_2$, 77136-39-1; $[Re(t\text{-}BuNC)_6][Cl]$, 77152-63-7; *trans*-$Ru(t\text{-}BuNC)_4(O_2CMe)_2$, 77136-40-4; $Rh_2(O_2CMe)_4(t\text{-}BuNC)_2$, 77136-41-5; $Mo_2(O_2CMe)_4$, 14221-06-8; $Mo_2(O_2CCF_3)_4$, 36608-07-8; $K_4Mo_2Cl_8$, 25448-39-9; $Mo_2Cl_4[P(n\text{-}Bu)_3]_4$, 39306-31-5; $Re_2(O_2CMe)_4Cl_2$, 14126-96-6; $Ru_2(O_2CMe)_4Cl$, 38833-34-0; $Rh_2(O_2CMe)_4(MeOH)_2$, 41772-64-9.

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Contribution from the Centro di Studio sulla Stabilità e Reattività di Composti di Coordinazione, CNR, Istituto di Chimica Analitica, and the Centro di Studio sui Biopolimeri, CNR, Istituto di Chimica Organica, 35100 Padova, Italy

Metal-Promoted Reactivity of Cyanogen toward Compounds Containing Active Hydrogen Atoms on Carbon. 2. Synthesis of a Fully Functionalized Substituted Pyrimidine from Cyanogen and Acetylacetone Catalyzed by Acetylacetonate Complexes of Transition Metals

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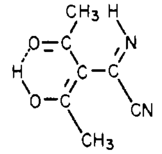
The reactivity of various metal acetylacetonate complexes $[M(acac)_n]$ ($n = 2$ for M = Mn^{II}, Fe^{II}, Co^{II}, Cu^{II}, Pd^{II}; $n = 3$ for M = Cr^{III}, Mn^{III}, Fe^{III}) has been tested toward C_2N_2 at ambient conditions in CH_2Cl_2. All $[M(acac)_2]$ complexes, except $[Pd(acac)_2]$, react with cyanogen to give addition compounds which are found to be unstable for Mn, Fe, and Co and quite stable for Cu. The Cu complex displays a stoichiometric composition $[Cu(acac{\cdot}C_2N_2)_2]$ and is found to be isostructural with the complex bis(3-(cyanoiminomethyl)-2,4-pentanedionato)nickel(II). Cr^{III} and Fe^{III} complexes are found to be unreactive in the employed conditions, and $[Mn(acac)_3]$ behaves similarly to $[Mn(acac)_2]$. The complexes found to be reactive with cyanogen are seen to be effective catalysts for the addition reaction of cyanogen to Hacac in mild conditions. On the basis of X-ray data, the organic compound obtained has been identified as a heavily functionalized pyrimidinic compound of stoichiometry $(Hacac{\cdot}C_2N_2)_2$. X-ray structure and IR, NMR, visible–UV, and mass spectra, referring to this novel compound, are given and discussed.

Introduction

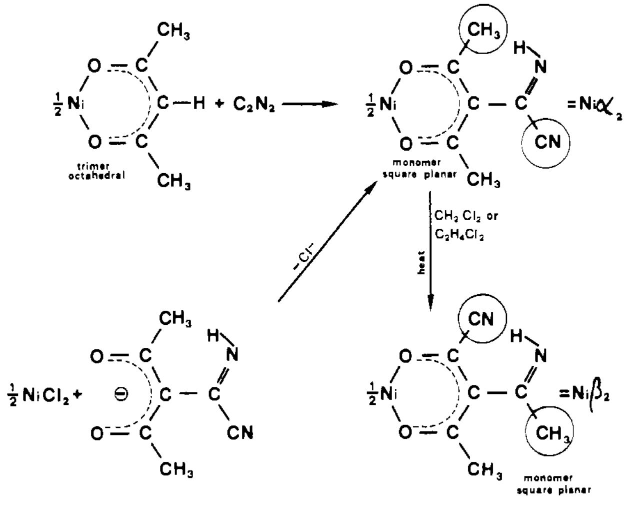
The reaction between cyanogen and acetylacetone at ambient conditions in ethanol in the presence of $C_2H_5O^-$ to give 3-(cyanoiminomethyl)acetylacetone (αH) has been described by Traube in 1899.[1c] Doubts on the correct identification of this compound have been advanced in the literature,[2] but very recent data published by us[3] confirm Traube's original proposal. It is worthwhile to underline the fact that the reaction does not occur thermally and it requires the presence of catalytic amounts of $C_2H_5O^-$.



αH

We have recently reported[4-6] that a compound with the minimal elemental composition $C_7H_8N_2O_2$, i.e., the same as that of αH, but with a completely different nature, can be obtained by reacting cyanogen and acetylacetone in CH_2Cl_2 at ambient conditions in the presence of catalytic amounts of $[Ni(acac)_2]$.

Scheme I



It is pertinent to point out that this organic synthesis was originated by an inorganic investigation, which led to the discovery[3-6] of a new "reaction mode" of cyanogen in its coordination chemistry.[7] We have found, in fact, that cyanogen, in addition to its behavior as an oxidative addition reagent and

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(1) (a) Instituto di Chimica Analitica. (b) Istituto di Chimica Organica. (c) Traube, W. *Chem. Ber.* 1898, *31*, 2938–2946.

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(3) Corain, B.; Del Pra, A.; Filira, F.; Zanotti, G. *Inorg. Chem.* 1979, *18*, 3523–3528.

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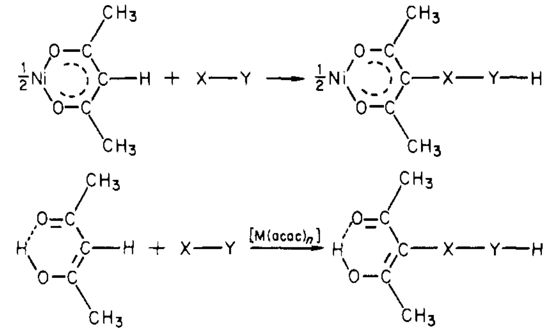
(7) For a review article on the subject see: Corain, B.; Basato, M.; Warsame, A. *Chim. Ind. (Milan)* 1979, *61*, 567–571.

Scheme II. Addition of Electrophiles to [Ni(acac)$_2$] and to Hacac



X–Y = R–N=C=O, $C_2H_5CO_2$–N=N–$CO_2C_2H_5$, $CH_3CO_2C{\equiv}CCO_2CH_3$

as a π-acidic Lewis base, can behave as an electrophile toward the nickel-coordinated 2,4-pentanedionate ligands (acac$^-$), giving an insertion reaction into the C–H methino bonds and, therefore, a novel complex containing two CN moieties per organometallic ring; see Scheme I.

Similar reactions at the metal-coordinated acac$^-$ moiety and similar addition reactions of various electrophiles, H–Y, to Hacac catalyzed by [M(acac)$_n$] complexes have been reported in the literature by Nelson et al[8] (Scheme II).

Remarkably, in these cases the addition of the electrophile to the coordinated acac$^-$ does not change the trimeric octahedral structure of the parent complex, while the corresponding reaction with C_2N_2 does. Moreover, the products of the metal-promoted organic syntheses were just those predictable on the basis of the insertion reaction of the electrophiles into the C–H methino bond of Hacac, while we will show in this paper that the product of the cyanation of Hacac is a novel organic compound arising from the metal-promoted dimerization of two Hacac·C_2N_2 moieties.

We will report in this paper our general results on the reactions between C_2N_2 and various [M(acac)$_n$] complexes, the catalytic consequences of these reactions, and the nature of the organic product obtained from the metal-catalyzed cyanation of Hacac.

Experimental Section

Most of the acetylacetonate complexes employed were from Merck Schuchardt and were used after a week-long treatment at 100 °C under vacuum. They were then stored at room temperature over P_2O_5; [Cu(acac)$_2$] and [Pd(acac)$_2$] were prepared by literature methods.[9] The solvents employed were reagent grade (Baker), and cyanogen was also a Baker reagent (98.5%, Union Carbide).

Conveniently concentrated solutions of C_2N_2 were prepared by sucking directly suitable amounts of the gas from the cylinder into the desired volume of CH_2Cl_2. The C_2N_2 concentration was determined as previously described.[10]

Addition reactions to various metallic substrates and the catalytic experiments were run in CH_2Cl_2, in closed vessels containing C_2N_2 at the desired concentration. The progress of the cyanation reaction of Hacac was followed by monitoring the Hacac concentration by means of gas chromatograms (Carbowax 20 M on Chromosorb W).

Catalysis experiments as well as preparative work concerning Co^{II}, Mn^{II}, and Fe^{II} were run under UPP argon (SIO).

Instruments. Routine spectra were recorded on a Perkin-Elmer 257 and the accurate ones on the 580 model. Electronic spectra were recorded on a Perkin-Elmer A 72, and magnetic susceptibilities were determined at room temperature on a Gouy apparatus employing a Bruker B-M 6 magnet coupled with a Sartorius electrobalance. NMR spectra were obtained on a Bruker WP 60 FT spectrometer at room temperature. Mass spectra data were obtained at the Centro Spettrometria di Massa of the University of Naples. Elemental analyses were performed in the microanalysis laboratories of our institutes.

Cyanation of [M(acac)$_2$] Complexes. Typically, 1–3 mmol of the metallic reagents were added to 50 cm^3 of CH_2Cl_2 containing an excess of C_2N_2 (generally a fivefold excess at room temperature). After 1 min of initial stirring, the solutions or suspension so obtained were left undisturbed for the required time.

In the case of [Cu(acac)$_2$] a procedure identical with that employed for the reaction of [Ni(acac)$_2$] was used[3] (reaction time ca. 6 h). The product is a brownish green microcrystalline material melting at 174 °C (Kofler), insoluble in petroleum ether, and slightly soluble in CH_2Cl_2, $CHCl_3$, and $C_2H_4Cl_2$. It can be recrystallized from hot $C_2H_4Cl_2$ to give a pure species analyzing correctly as [Cu($C_7H_7N_2O_2$)$_2$]. Anal. Calcd: C, 45.96; H, 3.85; N, 15.31. Found: C, 45.78; H, 3.94; N, 14.91. The yield was 40%. The IR spectra of the crude and recrystallized samples are identical. Remarkable bands: 3260 (s) (ν_{N-H}), 2220 (w) ($\nu_{C\equiv N}$), 1630 (s) ($\nu_{C=N}$), 1550 cm^{-1} (s) ($\nu_{C=O}$).

In the cases of [Fe(acac)$_2$] and [Co(acac)$_2$] the initially obtained red suspensions turned gradually to brown and, after 1 h, brown precipitates quite insoluble in the common organic solvents were obtained. Elemental analyses of these materials containing C, H, and N were erratic and not helpful. However, their IR spectra in Nujol mulls always displayed medium-strong $\nu_{C\equiv N}$ bands at 2180 (Fe) and 2185 cm^{-1} (Co) and other weak absorptions in the 2000–650-cm^{-1} range due to organic materials present in the crude products.

Quite similar results were obtained for [Mn(acac)$_2$] (initially a yellow suspension which led to a brown precipitate with a 2180-cm^{-1} IR band). For [Mn(acac)$_3$] a brown suspension was initially obtained, which turned slowly (24 h) to a reddish brown suspension. The filtered material resembled those isolated in the previous cases (band at 2175 cm^{-1}).

[Fe(acac)$_3$] and [Cr(acac)$_3$] gave dark red and violet solutions, respectively, which did not change color for 1 week. The metallic reagents could be recovered unchanged by evaporating the solutions after two days.

[Pd(acac)$_2$] initially gave a yellow solution, which very slowly turned to red. After 1 week, the IR spectrum of the solutions were the sum of those displayed by the reagents, and [Pd(acac)$_2$] could be recovered practically unchanged. The same results were obtained at 100 °C for some hours, by employing a 250-cm^3 stainless-steel autoclave.

Catalytic Addition of C_2N_2 to Hacac. The reaction was carried out in closed 100-cm^3 glass vessels to which Hacac (0.25–0.30 M), CH_2Cl_2 (ca. 20 cm^3), heptane (internal standard), and suitable amounts of conveniently concentrated stock solutions of C_2N_2 in CH_2Cl_2 (final concentration about 0.45 M) were added in the mentioned sequence. A combination of IR and GLC analyses was used to determine the C_2N_2 and Hacac concentrations.

The addition of the required amount of solid catalyst was performed by means of a conveniently arranged side arm (catalyst concentrations were normally 4×10^{-4} M, but for [Ni(acac)$_2$] some tests were run up to 10^{-3} M).

The addition of the catalyst generally caused no immediate visual effect, but with time a yellow or beige precipitate began to separate, while GLC analysis of the surnatant solutions revealed a catalytic engagement of Hacac. The final product was filtered off and examined as both crude and recrystallized (from CH_2Cl_2) material.

The crude materials obtained in any case display almost identical IR spectra and elemental analyses (see Table IV), all in agreement with the composition $C_7H_8N_2O_2$. A semiquantitative estimate of the mass balance revealed that the mass of the crude isolated product corresponded to that of Hacac and of C_2N_2 consumed in the reaction.

A very pure sample of the product (mp 220 °C, Kofler) was obtained by allowing a saturated CH_2Cl_2 solution to evaporate in an almost completely closed beaker for 3 months.

Yellow crystals suitable for X-ray analysis were obtained.

A very careful comparison of the IR spectra (Perkin-Elmer 580) of the crude samples (KBr disk) obtained from [Ni(acac)$_2$] and [Cu(acac)$_2$] as catalysts with that of the recrystallized sample employed for the X-ray, NMR, and mass spectrum showed that they all are identical.

X-ray Structure Analysis of I

Crystal data: $C_{14}H_{16}N_4O_4$, mol wt 304.11, monoclinic, a = 13.112 (7) Å, b = 10.639 (6) Å, c = 9.983 (6) Å, β = 94.0 (1)°, V = 1389.22 Å^3, ρ_o = 1.44 g cm^{-3}, ρ_c = 1.454 g cm^{-3} for Z = 4, F(000) = 624

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Table I. Atomic Coordinates ($\times 10^4$) of I, with Estimated Standard Deviations in Parentheses[a]

atom	x	y	z
O(1)	4565 (3)	7660 (4)	2888 (4)
O(2)	4569 (4)	8837 (4)	7117 (4)
O(3)	7409 (4)	3289 (4)	10169 (4)
O(4)	6249 (3)	5744 (4)	11154 (4)
N(1)	5827 (3)	6049 (5)	4125 (4)
N(2)	5687 (3)	6317 (5)	7688 (4)
N(3)	6694 (3)	5095 (4)	6299 (4)
N(4)	5125 (4)	7091 (5)	10095 (5)
C(1)	3378 (4)	7140 (6)	6924 (5)
C(2)	4282 (5)	7892 (6)	6522 (6)
C(3)	4740 (4)	7454 (5)	5252 (5)
C(4)	4339 (4)	8020 (6)	4016 (6)
C(5)	3626 (5)	9139 (6)	4073 (6)
C(6)	5468 (4)	6522 (5)	5243 (5)
C(7)	5969 (4)	5944 (5)	6490 (5)
C(8)	17191 (4)	4594 (5)	7367 (5)
C(9)	7992 (5)	3624 (6)	7128 (6)
C(10)	6962 (4)	4939 (5)	8670 (5)
C(11)	7575 (5)	4360 (6)	9839 (6)
C(12)	8468 (5)	5104 (7)	10415 (7)
C(13)	6185 (4)	5816 (5)	8770 (5)
C(14)	5856 (4)	6226 (6)	10127 (6)

[a] Coordinates of hydrogens are not listed.

e. Systematic absences $0k0$ when $k = 2n + 1$ and $h0l$ when $h = 2n + 1$ establish the space group as $P2_1/a$; λ(Mo K$\bar{\alpha}$) = 0.7107 Å.

Solution and Refinement of the Structure of I. Intensity data were collected from a platelike crystal, with dimensions ca. 0.08 × 0.20 × 0.22 mm, on a Philips PW 1100 four-circle diffractometer using a $\theta/2\theta$ scan mode (scan width = 1.1°, scan speed = 0.015° s^{-1}). A total of 2395 independent reflections were scanned in the 2θ sphere from 4 to 50°, with graphite-monochromatized Mo K$\bar{\alpha}$ radiation. Out of these reflections 1207 were considered to be observed at the 3σ level, as determined by counting statistics. Intensities were corrected for Lorentz and polarization effects and converted to an absolute scale by Wilson's method. Absorption and extinction corrections were ignored. The structure was solved by direct methods.[11] Full-matrix least-squares refinement of the positional and anisotropic thermal parameters of the nonhydrogen atoms converged to a conventional R factor of 0.055. Unit weights were applied. Hydrogens were located from a difference map but not included in the refinement. The scattering factors were taken from ref 12. The final values of the atomic coordinates are given in Table I. Bond lengths and angles are listed in Table II. The molecular arrangement with the atom numbering scheme used in the analysis is presented in Figure 1.

Physicochemical Properties of I

Visible–UV spectrum: λ_{max} at 242 and 372 nm with ϵ values 13 240 and 8350 M^{-1} cm^{-1}, respectively.

Infrared spectrum: remarkable bands at 3470 and 3440 (m–s), 3330 and 3265 (m–s), 1710 (m–s), 1690 (m–s), and 1620 cm^{-1} (m–s).

Mass spectrum: remarkable mass figures at 289, 272, and 230; parent ion peak at 304; molecular weight under high resolution conditions 304.1165 (theory 304.1171).

NMR spectrum. The compound is scarcely soluble in common organic solvents. In CH_2Cl_2 and $CHCl_3$ its solubility is about 10^{-3} M. The spectrum recorded in $CDCl_3$ at room temperature (4420 scannings) gave three peaks at τ 7.44, 7.74, and 7.80 with integration ratios 2:1:1 and two ill-defined very weak ones at τ ~2.7 and ~4.3. These last two peaks can be attributed to two kinds of N–H hydrogen atoms, while the first three peaks can be attributed to three different kinds of C(sp^3)–H hydrogens.

Results and Discussion

(A) Reaction of [$M(acac)_n$] complexes with C_2N_2.

The complexes tested for reactivity toward cyanogen in CH_2Cl_2 at room temperature were [$M(acac)_2$] (M = Mn, Fe, Co, Ni, Cu, Pd) and [$M(acac)_3$] (M = Cr, Mn, Fe). The data referring to [$Ni(acac)_2$] have been published separately, and some relevant features are summarized in Scheme I.

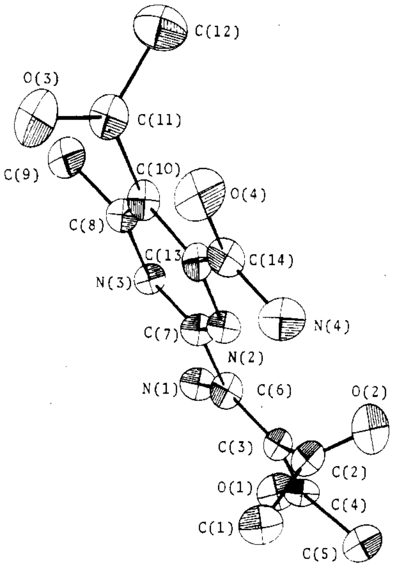

Figure 1. Single-crystal X-ray structure of I along with the atomic numbering system used in the analysis. The hydrogen atoms are not shown.

[$Cu(acac)_2$] is found to react with C_2N_2 as [$Ni(acac)_2$]. However, the primary reaction product does not behave as $Ni\alpha_2$ (see Scheme I) in that is is not converted by a recrystallization procedure into any isomeric species. A X-ray Debye analysis on the addition complex reveals that it is *isostructural with* $Ni\alpha_2$, and, therefore, we must assign it the $Cu\alpha_2$ "label".

$Cu\alpha_2$ exhibits a quite normal μ_{eff} value of 1.93 μ_B to be compared with the figures ranging from 1.8–2.0 μ_B for Cu^{II} β-diketoenolate complexes. Its spectrum in the visible region appears as a flat shoulder of a UV absorption ranging from 500 to 700 nm. The essential spectral data in the visible–UV region are reported in Table III (average figures of several independent measurements).

Solutions from 2×10^{-5} to 5×10^{-4} M obey the Lambert–Beer law in the visible–UV at room temperature.

In the cases of the other complexes, which react with C_2N_2, i.e., [$Mn(acac)_2$], [$Mn(acac)_3$], [$Fe(acac)_2$], and [$Co(acac)_2$], species similar to $Ni\alpha_2$, $Ni\beta_2$, and $Cu\alpha_2$ could not be isolated.

The infrared spectra of the solid products which precipitate spontaneously in these cases clearly indicate that these crude materials contain bridging cyanide ligands.[13] On considering the fact that the last mentioned complexes (with the exception of [$Fe(acac)_2$], which has not been tested) are effective catalysts for the addition of C_2N_2 to Hacac (see later), the hypothesis on the preliminary formation of species like $M\alpha_2$ or $M\beta_2$ seems fairly reasonable. We think that for Mn^{II}, Mn^{III}, Co^{II}, and Fe^{II} these species are unstable and evolve to metal cyanides and unidentified, but possibly interesting, organic materials.

[$Fe(acac)_3$] is found to be unreactive toward C_2N_2 after a contact time of 24 h and [$Cr(acac)_3$] and [$Pd(acac)_2$] were also found unreactive also after several days or weeks.

The presence of metal-coordinated cyanide ligands in the crude reaction products of manganese(II), manganese(III), iron(II), and cobalt(II) acetylacetonate with cyanogen appears to be, in any case, a remarkable finding in that it demonstrates that also complexes of metals in normal oxydation states can produce the rupture of the C–C bond in cyanogen,[7] very likely through the engagement of the previously coordinated ligand

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Table II. Bond Lengths (Å) and Angles (Deg), with Estimated Standard Deviations in Parentheses

C(2)-O(2)	1.215 (6)	C(6)-C(7)	1.499 (6)	C(8)-C(9)	1.504 (6)
C(1)-C(2)	1.507 (7)	C(14)-O(4)	1.227 (5)	N(2)-C(7)	1.336 (5)
C(2)-C(3)	1.514 (6)	C(14)-N(4)	1.327 (6)	C(7)-N(3)	1.334 (5)
C(3)-C(4)	1.440 (6)	C(14)-C(13)	1.515 (6)	N(3)-C(8)	1.322 (5)
C(4)-C(5)	1.517 (7)	C(11)-C(12)	1.495 (7)	C(8)-C(10)	1.404 (6)
C(4)-O(1)	1.244 (5)	C(11)-O(3)	1.209 (6)	C(10)-C(13)	1.390 (6)
C(3)-C(6)	1.377 (6)	C(11)-C(10)	1.503 (7)	C(13)-N(2)	1.333 (6)
C(6)-N(1)	1.339 (5)				

C(1)-C(2)-O(2)	122.1 (4)	C(12)-C(11)-C(10)	116.3 (4)
C(1)-C(2)-C(3)	115.2 (4)	O(3)-C(11)-C(10)	120.1 (5)
O(2)-C(2)-C(3)	122.5 (5)	C(6)-C(7)-N(2)	119.3 (4)
O(1)-C(4)-C(5)	117.5 (4)	C(6)-C(7)-N(3)	115.7 (4)
O(1)-C(4)-C(3)	123.4 (4)	N(2)-C(7)-N(3)	125.0 (4)
C(3)-C(4)-C(5)	119.0 (4)	C(9)-C(8)-N(3)	117.4 (4)
C(2)-C(3)-C(4)	116.5 (4)	C(9)-C(8)-C(10)	121.5 (4)
C(2)-C(3)-C(6)	122.9 (4)	N(3)-C(8)-C(10)	121.1 (4)
C(4)-C(3)-C(6)	120.5 (4)	C(11)-C(10)-C(8)	118.4 (4)
C(3)-C(6)-N(1)	124.1 (4)	C(11)-C(10)-C(13)	125.1 (4)
C(3)-C(6)-C(7)	123.6 (4)	C(8)-C(10)-C(13)	116.6 (4)
N(1)-C(6)-C(7)	112.3 (4)	C(14)-C(13)-C(10)	120.9 (4)
O(4)-C(14)-N(4)	124.8 (4)	C(14)-C(13)-N(2)	117.1 (4)
O(4)-C(14)-C(13)	119.8 (4)	C(10)-C(13)-N(2)	122.0 (4)
N(4)-C(14)-C(13)	115.4 (4)	C(13)-N(2)-C(7)	117.1 (4)
C(12)-C(11)-O(3)	123.0 (5)	C(7)-N(3)-C(8)	118.3 (4)

Table III. Visible-UV Spectral Data for $[Cu(acac\cdot C_2N_2)_2]$[a]

λ, nm	ε, M^{-1} cm^{-1}
253	19 400
291	30 300
342	4 500
415	4 500

[a] The IR Spectrum of $Cu\alpha_2$ is very similar to those of $Ni\alpha_2$ and $Ni\beta_2$[3] (particularly to that of $Ni\alpha_2$).

but possibly for Mn^{II}, Fe^{II}, and Co^{II} via the direct attack of C_2N_2 to the metal center.

Even though we cannot propose a reasonable explanation for the apparent instability of the (cyanoiminomethyl)acetylacetonate derivatives of Mn^{II}, Mn^{III}, Fe^{II}, and Co^{II}, we underline the fact that the lack of reactivity exhibited by $[Fe(acac)_3]$, $[Cr(acac)_3]$, and $[Pd(acac)_2]$ clearly indicates that a mechanism involving the direct attack of C_2N_2 to the C–H methino bonds of the coordinated $acac^-$ ligands has to be ruled out. If the activation process of cyanogen would occur, in fact, in the *direct attack to the C–H methino bond* on the various organometallic substrates (as it is proposed in ref 8 for various electrophiles), one would expect a gradual change in reactivity, if any, along the series of the employed substrates but *not* such a dramatic change on passing from the first-row $[M(acac)_2]$ species, e.g., from $[Cu(acac)_2]$ to $[Pd(acac)_2]$ and from $[Mn(acac)_3]$ to $[Cr(acac)_3]$ and $[Fe(acac)_3]$.

(B) Catalytic Cyanation of Hacac. Nature of "Hacac·C_2N_2". Besides $[Ni(acac)_2]$,[4-6] $[Mn(acac)_2]$, $[Mn(acac)_3]$, $[Co(acac)_2]$, $[Cu(acac)_2]$, and $Cu\alpha_2$ are found to be catalytically active for the addition of C_2N_2 to Hacac in mild conditions. Table IV collects some data referring to the catalytic process. The reported TN's (number of cycles) are not the highest to be obtained, and they only refer to experimentally convenient conditions.

Our experimental data leave little doubts on the fact that we obtained only *one kind* of product for all the catalysts employed and that byproducts, if any, have to be considered present only as traces.

It is worthwhile to mention that, while $[Ni(acac)_2]$ was found to give up to 100% conversion of Hacac to "Hacac·C_2N_2" in 24 h at concentrations somewhat greater than 10^{-3} M, for $[Co(acac)_2]$ and $[Mn(acac)_2]$ the figures reported in Table IV are not likely to be improved, apparently owing to the instability exhibited by the organometallic cyanation products, which, of course, have to play an essential role in the course of the catalytic process.

Table IV. Some Analytical and Catalytic Data on the Addition Reaction of C_2N_2 to Hacac in the Presence of Various $[M(acac)_n]$ (n = 2, 3) Complexes

catalyst	% anal. of organic products (crude samples)			no. of cycles (TN)	
$Ni(acac)_2$	54.07	5.29	17.97	370	[catalyst] = 4 × 10^{-4} M
$Cu(acac)_2$	55.42	5.63	18.18	332	$[C_2N_2]$ = 0.45 M
$Cu\alpha_2$	54.67	5.69	17.93	316	[Hacac] = 0.25 M
$Mn(acac)_2$	55.64	5.79	18.19	136	
$Co(acac)_2$				231	
$Mn(acac)_3$				93	reacn time 24 h
$C_7H_8N_2O_2$[a]	55.26	5.26	18.42		t = 26 °C
$Cr(acac)_3$				0	
$Fe(acac)_3$				0	
$Pd(acac)_2$				0	

[a] Theoretical.

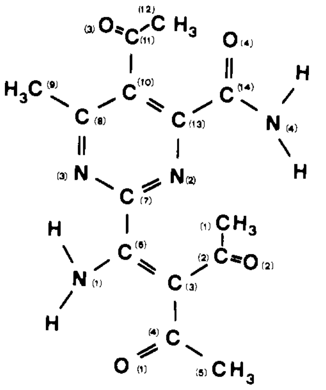


Figure 2. Canonical formula for $(Hacac\cdot C_2N_2)_2$ (I).

The plots of Hacac concentration vs. time revealed, in fact, a total inactivation of the system after 3 h for Co^{II} and 6 h for Mn^{II}.

(C) Crystal and Molecular Structure of I. The present X-ray analysis demonstrated unambigously that the obtained organic compound I is a heavily functionalized pyrimidine derivative, the canonical formula of which is reported in Figure 2, i.e., 2-(1′-amino-2′-acetyl-but-1′-enonyl)-4-carboxamido-5-acetyl-6-methyl-1,3-diazyne. The pyridine ring is planar within experimental error with all substituents significantly displaced from its mean plane. Bonding parameters within the ring (the

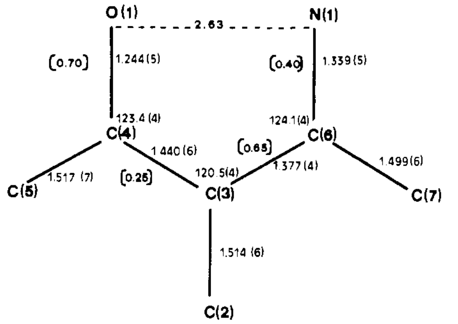


Figure 3. Dimensions of the conjugated system O(1)–C(4)–C(3)–C(6)–N(1). The amount of double-bond character calculated with Pauling's equation[14] is in brackets.

means of C–N and C–C bonds are 1.331 (5) and 1.397 (6) Å, respectively; the angles average 120.0 (4)°) are very close to the predicted ones from radii-sum rules in six-membered aromatic rings and are in agreement with those in observed structures of pyrimidine derivatives.[14]

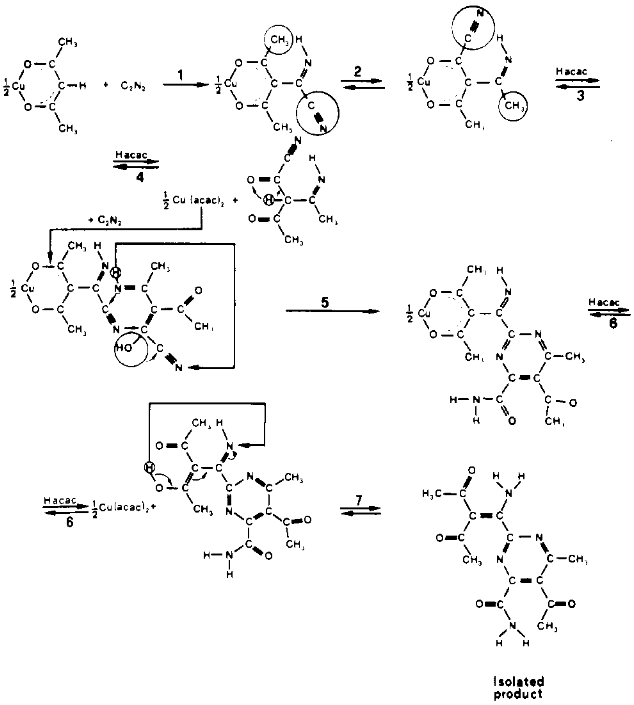
The values of the C(6)–C(7), C(10)–C(11), and C(13)–C(14) bonds compare well with a $C(sp^2)$–$C(sp^2)$ single bond.[14] This situation along with the significant deviations of the substituents from the mean-plane through the ring atoms and along with the rotation angles values about C(6)–C(7), C(10)–C(11), and C(13)–C(14) suggest that resonance does not extend from the pyrimidine ring to its substituent groups.

The C(13)–C(14)–O(4)–N(4) amide group is planar within the experimental error, and its dimensions compare well with those in observed structures of amide derivatives.[14] Bonding parameters of the three acetyl groups are quite normal.[14] In addition bond lengths and angles of the C(3)–C(4)–C(5)–O(1) and C(3)–C(6)–N(1) groups along with the approximate planarity of the O(1)–C(4)–C(3)–C(6)–N(1) system suggest that resonance would extend from N(1) to O(1) through C(6), C(3), and C(4), respectively. An important feature of this group is a very short N(1)···O(1) distance of 2.63 Å, which would indicate the presence of a strong intramolecular N–H···O hydrogen bond (Figure 3). N···O distances significantly shorter than frequently observed values[15] and justified only by the molecular geometry have been already reported.[16,17]

Organometallic Reaction Pathway for the Pyrimidinic Ring Closure Reaction. On the basis of the results concerning the structure of $M\alpha_2$ (M = Ni, Cu) and $Ni\beta_2$ and on the basis of the known structure of the organic reaction product, we propose here a *reaction* pathway able to justify the formation of the pyrimidinic ring (Scheme III).

Stage 1 is the straight cyanation of the coordinated $acac^-$ rings giving the $M\alpha_2$ species. This compound isomerizes to $M\beta_2$ in stage 2, and the attack of Hacac to the $M\beta_2$ species liberates 2-(1-iminoethyl)-1-cyano-1,3-butanedione (βH) and restores the catalyst in stage 3. Further attack of C_2N_2 to the catalyst gives again $M\alpha_2$ (stage 4), but free β H, in its enolic form, can attack the coordinated 3-(cyanoiminomethyl)-acetylacetonate to give (stage 5) a metal complex containing the pyrimidinic ring bound to a 3-(iminomethyl)acetylacetonate ligand.

Scheme III. Proposed Reaction Pathway for the Metal-Catalyzed C_2N_2 Addition to Hacac and for the Ring Closure Reaction



Further protonation of this last ligand liberates a tautomeric form of the final product (stage 6) and restores the catalyst. Equilibrium 7 leads to the isolated product, the lower solubility of which is likely to play an important role in the overall driving forces of the entire catalytic cycle.

Experimental support of the proposed reaction pathway is that $Cu\alpha_2$ catalyzes the cyanation of Hacac, giving (i) the same product and (ii) a very similar reaction rate (i.e., the same TN after the same time) in the same experimental conditions.

Synthetic Perspectives and Conlcusions. We have discovered a "one pot" synthesis of a novel pyrimidinic compound. The very mild conditions employed as well as the relatively low cost of the reagents leave little doubt of the opportunity to widely explore the synthetic perspectives of this metal-promoted catalytic synthesis, with the objective of preparing a series of highly functionalized pyrimidinic compounds, structurally related to I.

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Registry No. I, 77097-65-5; $Cu\alpha_2$, 77136-26-6; C_2N_2, 460-19-5; Hacac, 123-54-6; $Ni(acac)_2$, 3264-82-2; $Cu(acac)_2$, 13395-16-9; $Mn(acac)_2$, 14024-58-9; $Co(acac)_2$, 14024-48-7; $Mn(acac)_3$, 14284-89-0; $Fe(acac)_2$, 14024-17-0.

Supplementary Material Available: Table A (least-squares planes and dihedral angles), Table B (selected intramolecular nonbonded contacts), Table C (observed and calculated structure factors), Figure 4 (vis–UV Spectrum of I), Figure 5 (IR spectrum of I), and Figure 6 (mass spectrum of I) (15 pages). Ordering information is given on any current masthead page.

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